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Simplifying complex computer-generated reactions network to suppress its stiffness

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Abstract

Creation of mathematical model of complex radical processes manually is a very time-consuming process. Steam-cracking model created automatically by automated reaction network generation, on the other hand, becomes very large and complex for bigger molecules. This work was aimed at applying pseudo-steady state assumption automatically to components inside generated reactions network. The details of simplifying procedure are provided and the comparison of experimental data (lab-scale) to simulations by original and simplified model is presented. In overall, the simplification procedure lead only to marginal deviations in the simulated results, but the model ability to simulate bigger molecules has substantially improved.

Keywords: Reactions network generation; simplifying reactions network; steam-cracking modeling

1. Introduction

Modeling of steam-cracking process was initially limited to empirical approach but it is common knowledge that this approach limits possibility of model utilization. Mechanistic modeling of steam-cracking was initially focused on mechanism investigation and description of behavior of light individual components.

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There are several mechanistic models known from literature [1]. These models are usually based on mathematical description of known mechanism of radical decomposition that can be supplemented by a set of formal chemical reaction commonly replacing very complex part of mechanism. Mechanistic model is created and implemented manually for each component that is present in feedstock. In recent years, we also developed a model of industrial steam-cracking process [2]. It is obvious that the creating and implementing of mechanistic model of steam-cracking by hand, is very time-consuming process especially the implementing of radical decomposition kinetic description in cases of heavy components. Moreover, the flexibility of developed tool is limited when modeling of unusual feedstock steam-cracking is desired.

According to our former work [3], chemical reactions running during steam-cracking can be easily divided into several groups – types of chemical reactions. Each one of these reactions can be represented by a set of rules describing changes in reactant structure caused by the chemical reaction and these rules can be formalized by graph theory tools. This approach is usually called RNG (reactions network generation).

Froment et al published algorithms for generation of basic pyrolysis radical reactions and applied in cases of normal or branched paraffins [4]. They also recommended methods for kinetic parameters estimation based on active complex theory and quantum chemistry [5]. But there are no available papers comparing simulation to experimental data. This group continued their research by verifying assumptions like pseudo-steady state [6], the influence of radial temperature profile in tube reactor [7] etc.

Broadbelt et al [8] created a system by very similar approach. It is based on RNG using graph theory tools, kinetic parameters are calculated by “on-the-fly” quantum chemistry calculations.

Van Geem et al [9] were focused to description of steam-cracking of individual components and comparing to experimental data and models of simple mixtures [10].

Some works were obviously aimed at generation process rather than modeling or comparing to experimental data [8, 11]. Most of those works are interested in description only one component [9, 12] or simple mixtures [13] steam-cracking. If model is constructed more generally, comparison with experimental data for various feedstocks is missing.

Since our objective was the development of model for industrial application, it was critical for the model to be able to simulate steam-cracking of very different types of feedstock. Our aim was concentrated to development of steam-cracking kinetic model using RNG that would be able to describe various feedstocks. It was also needed to estimate kinetic parameters dynamically from structure of reactions network components.

2. Model description

Procedure of reaction network generation using graph theory tools has just been described in detail in [3] so we will describe structure of generated reactions network in this chapter because it is necessary to understand the principle of simplifying step. Generalized design of reactions network was created on basis of steam-cracking mechanism and kinetics research results [1, 5, 14].

Each molecule can be consumed by hydrogen-transfer chemical reaction. This reaction occurs predominantly on the carbon atoms that are not connected by multiple or aromatic bonds.

We have simplified description of this chemical reaction by following way. It has been investigated [6] that the level of attacking radicals can be considered to be pseudo-steady without any significant damage on model accuracy. Real hydrogen transfer is substituted by a simple scission; generated hydrogen radicals are “borrowed” and will be returned in recombination reaction to match the balance as written bellow. If we consider abstract active radical (RA), count of chemical reaction is significantly smaller

than in the case when every molecule can react with every radical in every possible position. This simplifying also reduces the stiff character of final system of differential equations.

Reality: $RH + R_A\bullet \rightarrow R\bullet + R_AH$

Model: $RH \xrightarrow{R_A\bullet} R\bullet + H\bullet$

C-H bond is attacked by an active radical. We have decided to use unified frequency factors for description of all these chemical reactions but activating energies are determined according to the count of alkyl substituents of attacked bond. Activating energy of H-transfer on the secondary carbon atom is considered to be a base, primary and tertiary carbon atoms are presented in the form of activating energy increments. If attacked bond is in the beta position to a double or aromatic bond(s), it is also considered as an increment to the base H-transfer activating energy. Concentration of active radical which is considered to be pseudo-steady is function of structure of reactants and reaction conditions. It is estimated by developed estimation method that has just been published and carefully tested by comparing of final conversion of different feedstock molecules under different conditions [3, 15].

Beta-scission reactions are divided by separate frequency factors to C-C and C-H scissions. It is obvious, activating energy of bond scission has to be dependent on the energy of the bond. The count of alkyl substituents influences activating energy again as well as the presence of double, triple or aromatic bond(s) in beta position.

In our former work, we found [15] it is necessary to distinguish C-C scission of bond that is a part of carbon cycle from the bond that is not. It is needed especially in the case when these reactions have the same reactant. Difference is caused by high probability of reverse reaction to scission of cyclic bond (intramolecular adition). This process reduces rate of cyclic bond scission and makes substituent cutting of more probable. Of course, we tried to implement an automatic generation of intramolecular adition during model development but we found that the count of chemical reactions steeply increased and the stiff character of system became to be too pronounced. That is the reason why system of cyclic bond scission and intramolacular adition was replaced by this corrective factor.

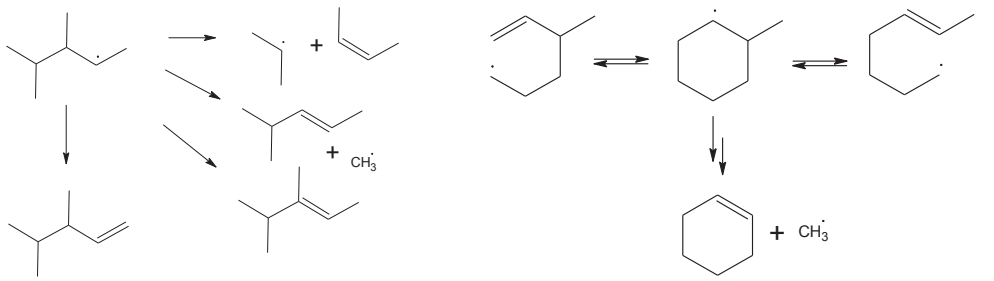

Fig. 1. (a) Demonstration of different β-scission possibilities; (b) Demonstration of cyclic bond scission influence reversibility

If there is no carbon cycle or multiple bond, isomerization of radical centre between 1,4 and 1,5 positions are included. Allyl-type radicals can also undergo the isomerization. Each one of these types of chemical reactions is reversible, having one frequency factor and activating energy.

Non-fissile radicals such as hydrogen and methyl or non-saturated short radicals, are very stable and can stay in reaction mixture for longer time therefore termination becomes significant. These radicals are

terminated in recombination reaction by the hydrogen radical. This reaction has also unified frequency factor and activating energy but this activating energy limits to zero in accordance with literature sources.

The last one type of generated chemical reactions is the reverse Diels-Alder reaction that can significantly influences products yields in specific cases of feedstock as we have recently presented [15]. Kinetic parameters of this type of chemical reaction are also unified.

For each one of reactant a group of consuming reactions is constructed. Their kinetic parameters are estimated and all reactions having selectivity under selected threshold (we use 1 %) are rejected. It limits the size of system within reasonable boundaries.

As written before, major concern is to generalize kinetic parameters and this approach allows us to generalize model for different types of feedstock. We optimized parameters of this model for laboratory experiments with selected substances using pyrolysis gas chromatography. There is no place on this paper to describe laboratory method but it was carefully described in recent paper [16]. Parameters were optimized as only one set of parameters as it was also presented [3, 15] for data obtained during experiments with following components:

- n-alkane: n-heptane
- i-alkanes: 2-methylheptane, 2,4-dimethylpentane, 2,2-dimethylpentane
- cycloalkanes: cyclopentane, cyclohexane
- substited cycloalkanes: methylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane

Reactor can be described to be an isobaric straight plug-flow tube reactor in steady state but velocity of reaction mixture is significantly increasing along the reactor, therefore concentration of components can not be explicitly divided. Balance equation of component *i* can be written as follow:

$$\frac{dJ_i}{dz} = \sum_{j \in reactions} r_j \nu_{j,i} \tag{1}$$

where J_i is the intensity of mole-flow, r_j is rate of chemical reaction j and $v_{j,i}$ is stochiometric coefficient of component i at reaction j. Rate equations are based on power low presuming all reactions are 1st-order to all its reactants represented by concentrations

$$r_j = k_j \cdot c_A \cdot c_B \tag{2}$$

where k_j is rate constant evaluated from Arrhenius eq. using parameters estimated by the method that was explain before and c are concentrations of corresponding reactants A nd B. Concentrations of reactants can be evaluated from mol-flow intensity using knowledge of reaction mixture velocity or total mixture volume-flow

$$c_A = J_A \cdot v = \frac{J_A}{\dot{V}} S \tag{3}$$

and reactor intersection S known from reactor geometry. We have explained system can be written explicitly for an explicit solver:

$$\frac{dJ_i}{dz} = k(T) \cdot c_A\left(J_A, \dot{V}\right) \tag{4}$$

It is needed to supplement the system of equations by description of volume-flow. We presumed ideal gas behavior:

$$\dot{V} = \frac{RT\dot{n}}{p} = \frac{RTS}{p} \sum_{i \in comp} J_i \tag{5}$$

Derivative of this expression can be quite complicated in dependence to count of variables that are depended on length coordinate *z*, in our case:

$$\frac{d\dot{V}}{dz} = \frac{RS}{p}\left(\frac{dT}{dz} \sum_{i \in comp} J_i + T \sum_{i \in comp} \frac{dJ_i}{dz}\right) \tag{6}$$

All elements used in this expression have just been evaluated. Temperature profile is based on geometry according to measured profile (instead of enthalpy balancing).

3. Simplification step

Model, as it has been presented, has quite strong STIFF character. It is cased by extreme differences between rate constants values. Therefore a special numerical solver has to be utilized for solution of the system. We have chosen Rosenbrock method [17]. But all similar methods have strong disadvantage: Jacobi matrix of the system is required. Generation of analytical expression of derivatives is very time-consuming process. Of course, derivatives can be evaluated numerically but numerical derivatives are determined with quite large deviations and its evaluation cost a lot of computer time. Using analytical or numerical derivatives the size of molecule to be simulated was capped at approximately 15 carbon atoms. When we tried to calculate simulations for larger size of feedstock molecule, count of components in reaction mixture naturally increased and the computer time increased unacceptably.

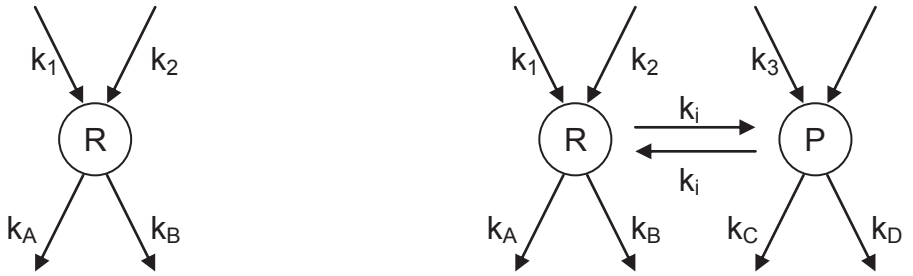

Fig. 2. (a) System of following chemical reactions with intermediate “R”; (b) system of following chemical reactions with two intermadiates (R, P) related by bidirectional isomerization, symbols k_i represent kinetic constants

As it is usual in modeling of radical processes, the stiff character is mostly caused by following chemical reactions where the first one is much slower the following one. As data from literature suggests [1], differences between rate constants (formation and decomposing of radical) are usually huge. Therefore we tried to apply pseudo-steady state assumption to radical intermediates. We can write expression for steady-state when sum of radical formation rate is equal to sum of radical decomposition rate but these analytical expressions must be applied in the right way to calculation would be effective.

When all participating chemical reactions are irreversible and all of following reactions are 1st-order to intermediate, the concentration of intermediate can be explicitly written (using designation from Fig. 2a):

$$c_R = \frac{r_1 + r_2}{k_1 + k_2} \tag{7}$$

Where r are rates of chemical reactions and k are rate constants with corresponding index. It can be generalized as portion of total formation rate of radical and sum of kinetic constants of reactions decomposing the radical.

But there are also reversible chemical reactions (radical isomerization) and in such cases there is no way how to express the intermediate concentration explicitly. But all these chemical reactions are also 1st-order and it can be written as simple system of linear eq. (using designation form Fig. 2b):

$$\begin{aligned} -\left(k_A + k_B + k_i\right)c_R + k_i c_P &= -\left(r_1 + r_2\right) \\ +k_i c_R - \left(k_C + k_D + k_i\right)c_P &= -\left(r_3 + r_4\right) \end{aligned} \tag{8}$$

It is only balance of presumption about equality of rates of formation and extinction that can be easily generalized again. If it is ordered in the same way like reaction networks (from reactants to products) expressions can be evaluated in the same order.

When reactions network is completed and model equations are needed to be generated, reactions network is searched component by component to the depth (DFS) from root(s) of reactions network and each component is evaluated. If it is the type of component in which case the simplification is enabled, it is investigated if this component is consumed by only 1st-order chemical reactions. If it is not, solution would involve non-linear equations. We have chosen not to apply this procedure in this case. But if it is, simplification can continue. If the component does not play any role in any reversible reaction, explicit expression for pseudo-steady concentration can be generated. If the component is connected by a reversible chemical reaction, all other components connected with this one are investigated. Expressions for steady-state for these components form a system of linear equations. Process continues by next components that have not been processed. Components that can not go throught simplification procedure are balanced by the way as was written in model description.

It is clear that this procedure separates subsystems that are independent and can be solved separately. Components that were processed by simplification procedure are no longer part of solution vector, their concentration are determined and can be used inside expressions in the rest of the system.

Table 1. Kinetic parameters obtained by the optimization of model to experimental data ([A] = s^{-1}, $m^3mol^{-1}s^{-1}$, [E] = [ΔE] = $J.mol^{-1}$)

Param. type	Chemical reaction and specif.	Value
A	H-transfer	3.62E08
E	H-transfer on primary carbon	26.69E03
E	H-transfer on secondary carbon	24.83E03
E	H-transfer on tertiary carbon	13.43E03
ΔE	H-transfer (allyl position)	-18.90E03
A	β-scission C-C (aliphatic bond)	1.38E19
A	β-scission C-C (bond in carbon cycle)	1.75E16
E	β-scission C-C (1 alkyl)	262.93E03
E	β-scission C-C (2 alkyl)	220.66E03
E	β-scission C-C (3 alkyl)	190.86E03
E	β-scission C-C (4 alkyl)	180.24E03
A	β-scission C-H	1.16E10
E	β-scission C-H (primary carbon)	168.32E03
E	β-scission C-H (secondary carbon)	118.45E03
E	β-scission C-H (tertiary carbon)	82.24E03
ΔE	β-scission (multiple bond in β position)	-10.29E03
A	Reconbination	1.00E10
E	Recombination	0.00E00
A	Allyl isomerization	4.50E11
E	Allyl isomerization	140.86E03
A	1,4-isomerization	9.71E10
E	1,4-isomerization	175.89E03
A	1,5-isomerization	4.39E09
E	1,5-isomerization	157.22E03
A	Reverse Diels-Alder reaction	3.19E08
E	Reverse Diels-Alder reaction	129.61E03

4. Results

Kinetic parameters obtained by model optimization may not match literature sources exactly, e. g. activating energy of H-transfer to primary and secondary carbon atom were determined to values 40.6 kJ/mol and 32.2 kJ/mol [1]. It is partially caused by the way how the H-transfer reaction is described.

Here we can show differences between products composition determined experimentally against simulation computed by original optimized model against the model utilizing simplification procedure (with the same values of kinetic parameters as the original one), for experiments with 3 very differently behaving feedstocks, see table 2.

Table 2. Comparison of conversion and reaction mixture composition (wt. %) under constant reaction pressure 4 Bar and carrier gas flow 100 Nml/min: experimental (exp.) vs. simulation using original model (sim1) vs. simulation using simplified model (sim2)

Item	n-heptane			2,4-dimethylpentane			1,2-dimethylcyclohexane		
T, °C	810			810			750		
	Exp.	Sim1	Sim2	Exp.	Sim1	Sim2	Exp.	Sim1	Sim2
Conversion	**87.68**	**87.84**	**87.84**	**92.95**	**91.74**	**91.68**	**41,90**	**41.70**	**41.63**
Hydrogen	0.88	0.93	0.93	0.89	0.64	0.64	0,90	0.52	0.53
Methane	7.13	9.28	9.27	11.75	11.88	11.88	3,94	3.20	3.20
Ethylene	48.08	46.73	46.73	9.85	9.96	9.96	5,83	6.67	6.66
Propylene	15.34	14.91	14.91	36.59	37.09	36.98	3,87	4.85	4.83
1-butene	5.10	0.57	0.57	3.47	4.99	5.01	0,93	1.29	1.29
2-butene	0.49	0.17	0.17	0.73	1.48	1.49	0,92	0.29	0.29
i-butene	0.08	0.00	0.00	13.39	13.67	13.67	0,15	0.00	0.00
Butadiene	4.21	5.94	5.93	3.62	2.38	2.39	4,72	3.30	3.30
C4	10.11	6.68	6.68	22.26	22.53	22.57	7,25	4.88	4.88
C5-C6	2.09	3.50	3.51	6.10	6.10	6.14	8,84	9.15	9.30
Benzene	0.38	1.34	1.34	1.45	0.05	0.05	1,77	0.42	0.41
Toluene	50.06	0.80	0.80	0.85	0.36	0.35	N/A	1.44	1.45

We can also show match of experimental values against simulations results for all components utilized for optimizations as was explained before, see Fig. 3

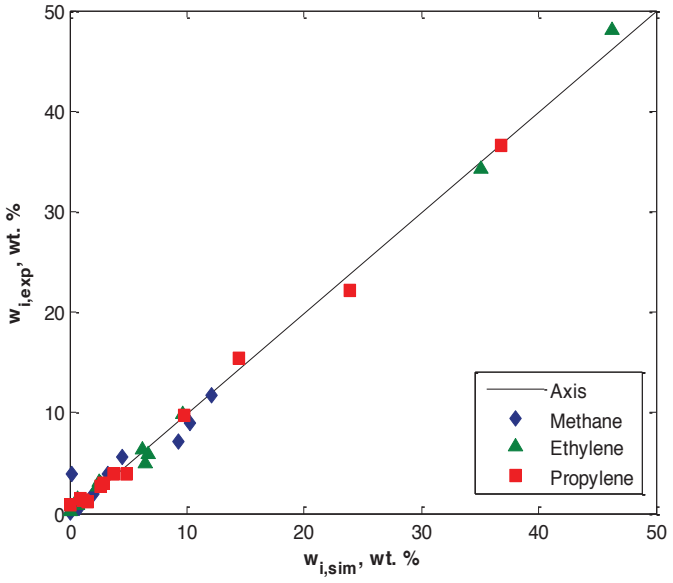

Fig. 3. Comparing experimental data to simplified model simulation computed using optimized kinetic parameters for different feedstocks (listed above) under variable conditions (700-810 °C, gas flow 50-200 Nml/min, p = 4 atm) following experimental

The table shows there are no significant differences between the simplified and original approach. However, the model ability to simulate cracking of larger molecules greatly improved. Alhough the computer time that is needed for solution of simplified model in cases C<9 is very similar to the time that was needed in original model case (seconds) but in cases of heavier feedstock differences become to be very significant. E.g. solution of n-dodecane model required about 20 minute now requires only 20 seconds. Model of n-tetradecane can be solved about 1 minute instead original 50 minutes. There is a fact that must be emphasized: all these models were generated with threshold of sensitivity 1 %. By reducing of this threshold, count of components in reaction system falls down as well as the computation time.

5. Conclusion

The existing automated reaction network generation model of steam cracking was extended by application of pseudo-steady state assumption on reactive radicals. This operation lead to substantial shortening of computation times for larger molecules and extended the limits of practical application for the model.

Deviations that were observed between solution of original optimized model and its simplified form are insignificant against total deviation between model and experiment and at least 1 order smaller than experimental deviations.

Pseudo-steady state applied to radicals heavier than C4 is acceptable for applied purposes of steam-cracking mathematical modeling.

Application of this presumption has significant effect to computation time in the cases of heavy feedstocks because there are many species in the reactions network for applying the presumption.

Acknowledgements

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